IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants:	Boris Bronfin, Eliahu Aghion, Frank von Buch, Soenke Schumann, Mark Katzir
Serial No.:	10/038,414
Filed:	January 3, 2002
Art Unit:	1742
Examiner:	I.P. Sikyin
For:	HIGH STRENGTH CREEP RESISTANT MAGNESIUM ALLOYS
Attorney Docket:	MM4501
Attorney:	Anderson, Kill & Olick, P.C. 1251 Avenue of the Americas New York, NY 10020-1182

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

DECLARATION OF PROF. BORIS BRONFIN

I hereby declare as follows:

1. I received Ph.D. and D.Sc. degrees from the Urals Polytechnic University in 1974 and 1988, respectively. Since that time I have been active in the field of physical metallurgy, particularly in the field of magnesium alloys. Based on numerous citations of my publications around the world, I was included in MARQUIS Who's Who in Science and Engineering, 2005-2006 (8th Edition), which distinguishes

scientists who are leading achievers in certain fields of Science and Engineering.

2. I have been employed by Dead Sea Magnesium Ltd since 1992. My current position is the head of Physical Metallurgy Department. The experiments included in this declaration were carried out under my direct supervision.

3. I am one of the co-inventors and co-applicants of the above identified application and I am familiar with the prosecution of this case. I have reviewed the following patent documents:

   - US 2001/0055539 to Nakamura et al. (denoted US/39 hereinafter);
   - JP 02047238 to Yamauchi et al. (denoted JP/38 hereinafter); and
   - US 6,139,651 to Bronfin et al. (denoted US/51 hereinafter).

4. The cited documents, like the instant application, deal with magnesium alloys, but they do not provide alloys with strength and creep resistance of our invention, as is shown below (par. 6-9).

   Magnesium alloys, being the lightest structural materials, have naturally many applications, and every application has different requirements on their physical and mechanical properties (ductility, strength, creep resistance, corrosion performance, fluidity in molten state, casting properties, thermal conductivity, etc.). Since most elements of the Periodic Mendeleyev Table are used in Mg alloys (see, e.g., Annex 1 – Avedesian, Table 4), finding a suitable composition, among so many combinations, with the required behavior for a given application is a matter of extensive experimentation. The number of factors affecting said behavior, nearly as high as the number of said element combinations, includes, e.g., solubility of metals, or the

formation of intermetallic compounds, whose presence radically changes the alloy properties. The formation of intermetallic compounds, as well as other factors, is affected in a very sensitive way by the presence of minor alloying elements, leading to a hardly predictable effects on the behavior.

A complex phase diagram of a simple mixture, containing only two components, can illustrate the complexity of the problems in this field (Annex 2 – Ullmann, Figure 1), especially when bearing in mind that usually more than five elements are present in a Mg alloy. These situations involve a multi-parameter problem; a combination of elements leading to certain properties cannot be relied upon in foreseeing the properties of another combination, even when the two combinations seem similar, because the extrapolation and prediction are not trivial, and sometimes are impossible to make. In practical situations, also costs of the materials must be taken into consideration.

5. Our invention provides alloys exhibiting high tensile and compressive yield strength combined with low creep rate at temperatures 150°C and higher, intended for applications such as making engine blocks or crankcases. Other properties, important during processing or using the alloys, were also born in minds by us when developing the instant alloys, and are related to in the specification of the application; however, tensile yield strength (TYS at 175°C) and minimum creep rate (MCR at 150°C under stress of 100 MPa) are mainly considered below in this declaration, in order to simplify the matter, and also because the two properties are included in the instant claims.

When considering other useful parameters for characterizing the behavior of the instant alloys, and in response to the Examiner's observations relating to TYS/UTS ratio, I would like to note that TYS values are not necessarily about 80% of UTS values; there are many examples of alloys having the same UTS but significantly different TYS. In the case of magnesium alloys it is well documented (for example in the internet site of the International Magnesium Association) that high ductility commercial alloys, such as AM50, AM60, and AE42, have TYS significantly lower than AZ91D alloy, but UTS the same or even higher than AZ91D.

The alloys of the cited Nakamura's document may be used as another example confirming my above observation. A data sheet, that has recently come to our attention, issued by Hitachi Company (to which the Nakamura's patent is assigned), shows two alloys designated Hitmag-A and Hitmag-B (Annex 4). A comparison with Nakamura's cited application shows that Hitmag-A corresponds to Alloy No. 8 and Hitmag-B to Alloy No. 2 from Table 1 of US/39. The data sheet shows TYS ("Proof Stress" in the table) values of 168 and 163 MPa, and UTS ("Tensile Strength" in the table) values 264 and 301, respectively, providing ratios 64% and 54%, i.e. significantly less than 80%. Nevertheless, as said above, we concentrate mainly on TYS and MCR values here.

6. Tables 2, 3 and 5 of the application contain chemical compositions of the alloys and their properties, respectively. Examples 1-14 have compositions in the ambit of the instant invention, and they show TYS (tensile yield strength) at 175°C greater than 150 MPa and MCR (minimum creep rate) at 150°C and 100 MPa less than $1.7x10^{-9}$/s (the two parameters are presented shortly, such as "150" and "1.7",

hereinafter). All these alloys further show good casting properties, higher than 85 when measured as combined castability rank (set during the R&D as the acceptability limit, castability rank is shown in Table 3 of the instant application). Comparative Examples demonstrate that the compositions deviating from the ambit of the invention, have inferior parameters at least in some of the measured features (Tables 2, 3, and 5). However, additional Comparative Examples (nos. 26-29) obtained during the development of the instant alloys, not included in the specification, are presented in this declaration in Table 2B, Table 3B and Table 5B (amended original Tables 2, 3 and 5) for the sake of clearer comparison with the cited prior art (attached as Annex 3).

7. Our alloys, denoted by symbol A_{our}, can be characterized by the presence of six elements, in a simple representation as follows:

A_{Our} = Al<4.7 - 7.3>
Mn<0.17 - 0.60>
Ca<1.8 - 3.2>
Sn<0.3 - 2.2>
Zn<0 - 0.8>
Sr<0 - 0.5>

wherein the numbers represent ranges of the elements in wt%, non-magnesium elements being limited to maximally 14.6 wt% (claim 1).

Nakamura's alloys, A_{Nak}, of US/39, may be presented as follows:

A_{Nak}= Al<2 - 20>
Mn<0.05 - 1.5>
(Ca or Si or RE)<0 - 5>
Sn<0.1 - 15>
Zn<0.1 - 10>
(Sr or Sb)<0 - 1>

wherein Ca in Nakamura may be replaced by Si or by rare earth (RE), and Sr may be replaced by Sb, non-magnesium metals being possibly 2.2 - 52.5 wt% (claims 1 and 9 of US/39).

In view of broad ranges of elements in the claimed compositions of US/39, further combined with 8 possible selections for Ca or Si or RE (no of them, or one of them, or two of them or all of them), and 4 possible selections for Sr or Sb, yielding 32 combinations for Ca/Sr group, it may be difficult to cover all combinations allowable in Nakamura; however, below we present two comparative examples in the ambit of US/39, Examples 26 and 27 (Annex 3). Both have Al content typical for Nakamura's exemplified alloys (e.g., Table 1 in the cited US application), the former having all the elements (except for said Al) as close as possible to our optimal composition, and the latter having the elements close to the Nakamura's optimal values, as taught in Nakamura's Table 1 and the Figures. Our Example 9, near to our "optimal composition" (i.e. a composition showing very good TYS and MCR values) is presented for comparison:

A_{Ex9}= Al(5.9)
Mn(0.26)
Ca(3.0)
Sn(0.5)
Zn(0)
Sr(0.3)
TYS(172)
MCR(0.75)

A_{Ex26}= Al(11.8)
Mn(0.22)
Ca(2.9)
Sn(0.45)
Zn(0.05)
Sr(0.28)
TYS(124)
MCR(198)

A_{Ex27}= Al(12.1)
Mn(0.19)
Ca(0)
Sn(4.9)
Zn(3.2)
Sr(0)
TYS(121)
MCR(322)

A_{Ex26} represents an alloy having five of six ranges near to our "optimal composition", with the sixth one (Al) deviating from our ambit. TYS and MCR values demonstrate that varying one element, remaining within Nakamura's ambit but leaving our ambit, led to sharp retreat from the required properties. It might be argued that there are more "optimal combinations", or "good combinations", within the Nakamura's ambit, and that a simultaneous variation of other elements might provide good results. However, said argumentation is contested by A_{Ex27}, in which not only Al but all ranges are selected according to the best of Nakamura's knowledge and experience, and TYS and MCR values are still farther from the required properties. Theoretically, if the above argumentation had been proven correct by enormously excessive experimentation (i.e., if proven that the broad Nakamura's range comprises several range combinations that provide superior results), it would only corroborate the inventiveness of our selection, in view of the required excessive effort.

The Examiner notes that the claimed creep rates and tensile properties might be inherently possessed by the materials of the cited references. The above two examples show that it is not the case. We could choose other examples of element combinations from Nakamura's ambit that deviate more strikingly from our ranges, but we believe that the above two examples sufficiently demonstrate our point; whether deviating in one element (Al) or four elements (Al, Zn, Ca, Sn), an alloy will not easily attain our required properties; our claimed special ranges, however, provide our required properties. As said, it might be argued that other examples, deviating from our ranges differently, e.g. otherwise than in Al, would show that our claimed range is not the only selection providing good results. However, Nakamura's teaching is that 12 wt% Al or more is good for strong alloys (e.g., Fig. 8), and lower

values are bad. In order to come to our composition, Bronfin's lower Al would have to be combined with Nakamura's high calcium (selected from among three possible elements), and a medium amount of Sn would have to be added (missing in Bronfin and being too high in Nakamura).

Bronfin's alloys, A_{Bro}, in US/51, may be presented as follows:

A_{Bro}= Al<4.5 - 10>
Mn<0.15 - 1.0>
Ca<0.2 - 1.2>
Sn<0>
Zn<0.01 - 1>
Sr<0.01 - 0.2>
RE<0.005 - 0.015>

Comparative Examples 28 has a composition in the ambit of US/51, but as close as possible to our "optimal" alloy of Example 9, whereas Comparative Example 29 has a composition comprising typical values as taught in Bronfin (e.g., Table 1, US/51) for all the elements, except for Ca which is chosen to be 3 wt%, i.e. outside the ambit of US/51, to improve the alloy according to the present application.

A_{Ex28}= Al(5.9)	A_{Ex29}= Al(7.1)
Mn(0.33)	Mn(0.32)
Ca(1.15)	Ca(3.1)
Sn(0)	Sn(0)
Zn(0.01)	Zn(0.74)
Sr(0.18)	Sr(0.21)
RE(0.05)	RE(0.15)
TYS(88)	TYS(150)
MCR(115)	MCR(2.3)

Although the addition of Ca improves the properties substantially, none of the two examples has the properties as claimed in the present application (not mentioning inferior castability ranks, Table 3B). In order to get the claimed values (and good castability), Sn would have to

be added, and probably RE taken out, which are, however, changes not obvious from the cited documents.

Yamauchi's alloy, A_{Yam}, in JP/38 may be presented as follows:

A_{Yam}= H
(Al or Mn or Ca or Sn or Zn or Sr or Zr or Sb or Bi or Co and/or 15 other elements)<0 - 10>

Comparative Example 30 has a composition in the ambit of JP/38, but without hydrogen or any element exotic for our composition (which would worsen the properties), and with the values not far from our values. In fact, Comp. Ex. 30 represents a composition, which (except for "exotic elements") is not far from any of the ambits of the three cited documents.

A_{Ex30}= Al(8.9)
Mn(0.23)
Ca(0.56)
Sn(0.2)
Zn(0.79)
Sr(0)
TYS(110)
MCR(92)

It can be seen that this "neutral" composition, not far from any of the cited documents, and not so far even from our composition, is not even close to our claimed properties.

I think that the examples show that if a skilled person (without knowing our instant application) had selected from the possibilities provided by A_{Nok}, A_{Bro}, and A_{Yam} a combination that would be near to the ranges taught by the publications, the claimed values of TYS and MCR would not be automatically (inherently) obtained. I further believe that the examples show that if said skilled person had

incidentally chosen a combination close to our "optimal combination", he would not get our claimed values of TYS and MCR, even if equaling our combination in five of the six ranges. Finally, as an alloy developer I know that attempts to reproduce published recipes and combine them may often lead to desperately branched web of futile trials. In one aspect, our alloys contain a certain quadruplet of obligatory chemical elements, which may constitute up to 14.6%, US/39 alloys contain a different quadruplet (necessary elements, according to claim 1), constituting to 46.5%, US/51 alloys contain a certain heptaplet, constituting not more than 17%, and JP/38 alloys contain only one obligatory element as follows:

A_{Our}	=	Al, Mn, Ca, Sn	[14.6%]
A_{Nak}	=	Al, Mn, Zn, Sn	[46.5%]
A_{Bro}	=	Al, Mn, Ca, Zn, RE, Be, Sr	[17%]
A_{Yam}	=	H	[?]

It am not aware of any standard method known in the art, which would enable to combine $A_{Nak} + A_{Bro} + A_{Yam}$ to get A_{Our}.

The strength and creep rate values of the Comparative Examples 26-30 (as well as of Comparative Examples filed with the application) depart from the required values, in most cases strikingly, which I believe to demonstrate the difficulty of using the cited documents for deducing the composition of our alloys.

8. I would not include JP/38 among prior publication considered in combining prior art knowledge and developing new materials, and I believe that another skilled person would not do so either. Inoculating the alloy with hydrogen according to JP/38 would spoil any properties which are desired for our instant applications (strength, high temperature applications, etc.). E.g., it is known that hydrogen reduces

substantially strength (e.g., www.key-to-metals.com). JP/38 is intended for totally different application – namely for vibration damping.

I would not select this document among information sources for my R&D anyway, because among many combinations falling into the ambit of the document, there are combinations problematic from viewpoint of metallurgic science, such as metals combinations known to be incompatible. Some of the mixtures within the ambit of JP/38 would not provide alloy, and due to limited solubility, would produce a heterogeneous mixture. I believe that a skilled person would understand this problem, and such knowledge would naturally cast doubts on usefulness of other mixtures provided by this publication. For example, the following doublets of metals comprised in JP/38 provide insoluble interfacing elements in molten magnesium: Al-Zr, Ca-Sb, Co-Zr, Mn-Zr, Si-Zr (Annex 1, Table 5).

9. I believe that Comparative Examples 26 and 27 demonstrate that Nakamura does not make our ranges obvious. A "typical", average composition according to the cited document, such as Comp. Ex. 27, is very far from the instant alloys both in strength and in creep rate, when compared under the same conditions; however, even a composition as close to the instant alloys as allowed by the ambit of the cited document, does not provide much better results, as Comp. Ex. 26 demonstrates. Comparative Examples 28 and 29 demonstrate that US/51 does not make our ranges obvious either. Comp. Ex. 28 is a composition in the US/51's ambit, but as close to the instant alloys as possible; Comp. Ex. 28 does not exhibit the claimed properties. "Improving" US/51 alloys by jumping out of the ambit of US/51, and by adding more Ca, as in Comparative Ex. 29, improves the alloy, but not enough to make it equal to the instant alloys. Comparative Ex.29 has

also very poor castability. Comparative Example 30, although prepared without hydrogen or other 15 elements allowable according to JP/38, does not conform to the claimed properties either.

I believe that the above examples, together with those already presented, demonstrate that the published element combinations cannot be obviously combined to provide the strength and creep rate that we claim in our instant application.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made herein on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the subject application or any patent issuing thereon.

Dated 5/05/05 Boris Bronfin

ANNEX 1

ASM Specialty Handbook®

Magnesium and Magnesium Alloys

Edited by
Michael M. Avedesian
Noranda Magnesium Inc.
and
Hugh Baker
ASM International (Retired)

Prepared under the direction of the
ASM International Handbook Committee

ASM International Staff
Steven R. Lampman, Technical Editor
Grace M. Davidson, Manager of Handbook Production
Bonnie R. Sanders, Manager of Copy Editing
Alexandra B. Hoskins, Copy Editor
Kathleen S. Dragolich, Jill A. Kinson, and Candace K. Mullet, Production Coordinators
Scott D. Henry, Assistant Director of Reference Publications
William W. Scott, Jr., Director of Technical Publications

The Materials
Information Society

First printing, May 1999

Library of Congress Cataloging-in-Publication Data

Magnesium and Magnesium Alloys/
edited by Michael M. Avedesian and Hugh Baker

Prepared under the direction of the ASM International Handbook Committee
p. cm.—(ASM Specialty Handbook)

Includes bibliographical references and index
1. Magnesium handbooks, manuals, etc. 2. Magnesium alloys Handbooks, manuals, etc.
I. Avedesian, M. M. II. Baker, Hugh. III. ASM International. Handbook Committee.
IV. Series.
TA480.M3M32 1999 99-20208
669'.732—dc21
ISBN: 0-87170-657-1
SAN: 204-7586

ASM International®
Materials Park, OH 44073-0002

Printed in the United States of America

Table 4 Liquid solubility and alloying efficiency of alloying additions to magnesium

Added element	Form of addition	Apparent liquid solubility, %	Alloying efficiency, %
Aluminum	Metal	100	90–100
Antimony	Metal	100	100
Arsenic	Metal granules		60–100
Barium	Metal	100	25–100
Beryllium	Al-Be	0.01	10–30
	$BeCl_2$		
Bismuth	Metal	100	100
Boron	BCl_3		<5
	Metal Powder		
Cadmium	Metal	100	100
Calcium	80Ca-20Mg	100	50–100
	Metal		
Cesium	Metal sealed in glass ampule		0 (contained 0.23 Si)
Chromium	Metal	0.01	0–8
	Metal powder		
	$CrCl_3$		
Cobalt	Metal powder	~5	1–100
	Metal turnings		
	Metal		
Copper	Metal	100	100
Gallium	Metal shot	100	85–100
Germanium	Metal	100	70–100
Gold	Metal	100	100
Indium	Metal	100	95–100
Iodine	I_2		0
Iron	Metal powder	~0.1	10
	Metal turnings		
	$FeCl_3$		
Lead	Metal	100	100
Lithium	Metal	100	95
Manganese	$MnCl_2$	~5.0	75
	$MnCl_2$ as #250 flux		
	Al-Mn		
	Mn powder		50–90
	Mn platelets		50–90
Mercury	Metal	100	70
Mischmetal (RE metals)	Metal	100	80–100
	REF_3 and $RECl_3$		
Molybdenum	$MoCl_4$	≥1.0	100
			0–45
	Metal powder		
	Metal		
Nickel	Metal	100	100
Niobium	Metal	0	0
	Metal powder		
Osmium	Metal powder		58
Palladium	Metal	100	100
Phosphorus	Fe_2P	~0.01	0–60
Platinum	Metal	100	100
Potassium	Metal	~0.02	5–15
Rhodium	Metal	~0.5	100
Rubidium	Metal sealed in glass ampule	0	0 (contained 0.10 Si)
Ruthenium	Metal powder	≥0.003	<1
Samarium	Mixture of RE metals	0	0
Selenium	Metal		0–38
Silicon	FeSi (95% Si)	100	35–85
	Metal powder		
Silver	Metal	100	100
Sodium	Metal	~0.1	10–80
Strontium	Metal	100	30–100
Tantalum	Metal	~0.015	0
	Metal powder		0–1.5
Tellurium	Metal	~0.2	20–50
Thallium	Metal	100	95–100
Thorium	Metal	100	75–100
	ThF_4 and $ThCl_4$		
Tin	Metal	100	100
Titanium	Metal	≥1.0	0–100
	$TiCl_4$		10
Tungsten	Metal	≥0.2	0–21
	Metal powder		
Uranium	Metal		<10
Vanadium	Metal powder	≥0.02	0
	VCl_4		
Yttrium	REF_3 mix		~0
Zinc	Metal	100	95–100
Zirconium	Metal	0.95	20–50

Effects of Alloying Constituents

The physical properties of magnesium are, of course, affected by the amount of each alloying constituent added to it. In many instances, the effect is more or less directly proportional to the amount added, up to the limits of solid solubility at the temperature at which the property is measured (see Fig. 3). The processing and property effects of the individual alloying elements, however, are more important in most structural applications than the physical properties. Descriptions of these effects follow for the elements commonly used in commercial magnesium alloys.

Aluminum has the most favorable effect on magnesium of any of the alloying elements. It improves strength and hardness, and it widens the freezing range and makes the alloy easier to cast. When present in amounts in excess of 6 wt%, the alloy becomes heat treatable, but commercial alloys rarely exceed 10 wt% aluminum. An aluminum content of 6% yields the optimum combination of strength and ductility.

Beryllium. Although only slightly soluble in magnesium, adding up to about 0.001 wt% beryllium decreases the tendency for the surface of the molten metal to oxidize during melting, casting, and welding. It can be used successfully in die-cast and wrought alloys, but must be used judiciously in sand-casting alloys because of its grain-coarsening effect.

Calcium is a special alloying ingredient added in very small amounts by some manufacturers to assist in metallurgical control. It serves a dual purpose: when added to casting alloys immediately prior to pouring, it reduces oxidation in the molten condition as well as during subsequent heat treatment of the casting, and it improves the rollability of magnesium sheet. The addition of calcium must be controlled to below about 0.3 wt%, however, or the sheet will be susceptible to cracking during welding.

Copper adversely affects the corrosion resistance of magnesium alloys if present in quanti-

Table 5 Interfacing elements in molten magnesium

Al-Ba	Fe-Li
Al-Co	Fe-Zr
Al-Fe(a)	Li-MM-Mn
Al-Mo(a)	Li-Mn
Al-MM-Li	Li-Ni
Al-Ni	Li-Sb
Al-Th	Li-Th
Al-Zr	Li-Zr
B-Fe	MM-Sb
B-Mn	MM-Si
Be-Fe	Mn-Si
Be-Mn	Mn-Zr
Be-Zr	Ni-Zr
Bi-Ca	Pb-Zr
Bi-Li	Sb-Th
Ca-Sb	Sb-Zr
Co-Zr	Si-Th
Cu-Li	Si-Zr

Note: Other compounds have been reported that, when each element is considered individually, would be expected to be soluble in molten Mg. Some of these high-melting compounds probably would not be soluble in molten Mg. (a) Probably a ternary combination

ties exceeding 0.05 wt%. However, it improves high-temperature strength.

Iron is one of the more harmful impurities in magnesium alloys in that it greatly reduces the corrosion resistance if present in even small amounts. In ordinary commercial-grade alloys, the iron content can average as high as 0.01 to 0.03 wt%. For maximum resistance to corrosion, however, 0.005% is specified as the upper limit for iron content.

Lithium has relatively high solid solubility in magnesium (5.5 wt%, 17.0 at.%), and because of its low relative density of 0.54, it has attracted interest as an alloying element in magnesium alloys to lower the density to values even lower than that of unalloyed magnesium. Moreover, only some 11 wt% of lithium is needed to form the β phase, which has a body-centered cubic (bcc) crystal structure (rather than a hexagonal close-packed, or hcp, structure), thereby improving formability of wrought products. The addition of lithium decreases strength, but increases ductility. Mg-Li alloys are also amenable to age hardening, although they tend to overage at only slightly elevated temperatures (e.g., 60 °C, or 140 °F). So far, Mg-Li alloys have found only limited application.

Manganese does not have much effect on tensile strength, but it does increase yield strength slightly. Its most important function is to improve the saltwater resistance of Mg-Al and Mg-Al-Zn alloys by removing iron and other heavy-metal elements into relatively harmless intermetallic compounds, some of which separate out during melting. The amount of manganese that can be added is limited by its relatively low solubility in magnesium. Commercial alloys containing manganese rarely contain over 1.5 wt%, and in the presence of aluminum, the solid solubility of manganese is reduced to about 0.3 wt%.

Nickel is like iron in that it is another of the more harmful impurities in magnesium alloys because it also greatly reduces the corrosion resistance if present in even small amounts. In ordinary commercial-grade alloys, the nickel content can average as high as 0.01 to 0.03 wt%, but for maximum resistance to corrosion, 0.005% is specified as the upper limit for nickel content.

Rare earth metals are added to magnesium alloys either as mischmetal or as didymium. Mischmetal is a natural mixture of the rare earths containing about 50 wt% cerium, the remainder being principally lanthanum and neodymium; didymium is a natural mixture of approximately 85% neodymium and 15% praseodymium.

Additions of the rare earths increase the strength of magnesium alloys at elevated temperatures. They also reduce weld cracking and porosity in casting because they narrow the freezing range of the alloys.

Silicon. The addition of silicon to magnesium alloys has been found to increase fluidity of the metal in the molten state. However, it decreases corrosion resistance of magnesium alloys if iron is also present in the alloy.

Silver additions improve the mechanical properties of magnesium alloys by increasing response to age hardening.

Thorium additions increase the creep strength of magnesium alloys at temperatures up to 370 °C (700 °F). The most common alloys contain 2 to 3 wt% thorium in combination with zinc, zirconium, or manganese. Thorium improves the weldability of alloys containing zinc.

Tin is useful when alloyed with magnesium in combination with small amounts of aluminum. The tin serves to increase the ductility of the alloy and makes it better for hammer forging because it reduces the tendency for the alloy to crack while being hot worked.

Zinc is next to aluminum in effectiveness as an alloying ingredient in magnesium. Zinc is often used in combination with aluminum to produce improvement in room-temperature strength; however, it increases hot shortness when added in amounts greater than 1 wt% in magnesium alloys containing 7 to 10 wt% aluminum. Zinc is also used in combination with zirconium, rare earths, or thorium to produce precipitation-hardenable magnesium alloys having good strength. Zinc also helps overcome the harmful corrosive effect of iron and nickel impurities that might be present in the magnesium alloy.

Zirconium has a powerful grain-refining effect on magnesium alloys. It is thought that because the lattice parameters of α-zirconium (a = 0.323 nm, c = 0.514 nm) are very close to those of magnesium (a = 0.320 nm, c = 0.520 nm), zirconium-rich solid particles produced early in the freezing of the melt may provide sites for the heterogeneous nucleation of magnesium grains during solidification.

Zirconium is added to alloys containing zinc, rare earths, thorium, or a combination of these elements where it serves as a grain refiner (up to its limit of solid solubility). However, it cannot be used in alloys containing aluminum or manganese because it forms stable compounds with these elements and is thus removed from solid solution. It also forms stable compounds with any iron, silicon, carbon, nitrogen, oxygen, and (mainly) hydrogen present in the melt. Because only the portion of the zirconium content available for grain refining is that which is in solid solution, the soluble zirconium content, rather than the total zirconium content, is the value important to the alloy.

Yttrium has a relatively high solid solubility in magnesium (12.4 wt%) and is added with other rare earth elements to promote creep resistance at temperatures up to 300 °C (570 °F). About 4 to 5% Y is added to magnesium to form commercial alloys such as WE54 and WE43, where it imparts good elevated-temperature properties up to about 250 °C (480 °F).

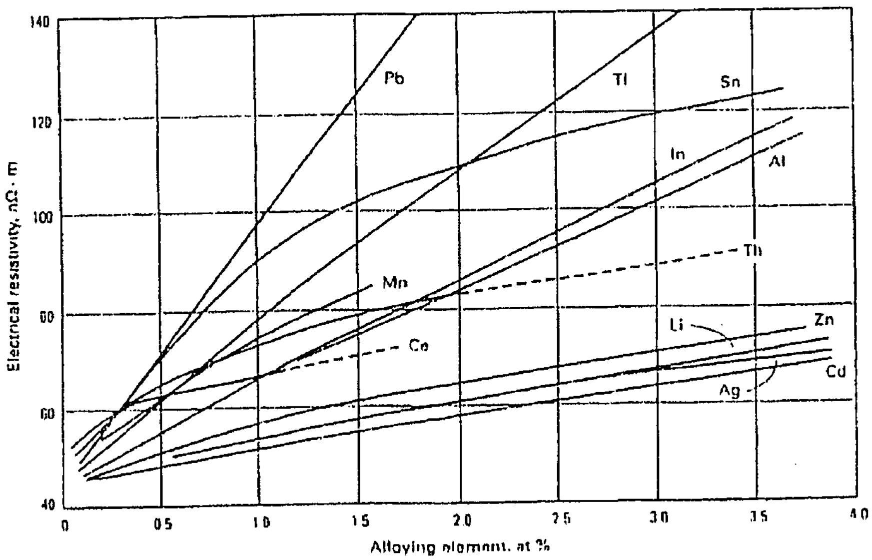


Fig. 3 Effect of alloying additions on the electrical resistivity of magnesium. Source: Ref 12, 13

Commercial Alloy Systems

The five basic groups of alloy systems that are currently being commercially produced are based on the major alloying elements: manganese, aluminum, zinc, zirconium, and rare earths. These are subdivided as follows:

- Magnesium-manganese
- Magnesium-aluminum-manganese
- Magnesium-aluminum-zinc-manganese
- Magnesium-zirconium
- Magnesium-zinc-zirconium
- Magnesium-rare earth metal-zirconium
- Magnesium-silver-rare earth metal-zirconium
- Magnesium-yttrium-rare earth metal-zirconium

ANNEX 2

This is a reprint of an article from the fifth edition of

Ullmann's Encyclopedia of Industrial Chemistry

Ullmann's has a long and successful tradition. The first compilation of its kind appeared in 1914 and its fourth edition was completed in 1984
The fifth edition is a complete revision, written entirely in English. Its Editorial Advisory Board includes leading scientists and engineers from the major industrial countries. Articles enjoy international authorship, and reflect industrial practice and know-how worldwide, making Ullmann's Encyclopedia of Industrial Chemistry the unique reference source.
This reprint typifies the concise and amply illustrated articles. Each contribution is meticulously edited to maintain clarity and uniformity throughout the 36 volume series. Ullmann's Encyclopedia of Industrial Chemistry serves readers in all branches of the chemical and allied industries around the world

If you wish to obtain further information, please write to VCH Verlagsgesellschaft, P O Box 101161, D-69451 Weinheim, Federal Republic of Germany Customers in the USA and Canada should write to VCH Publishers, Suite 909, 220 East 23rd Street, New York, NY 10010-4606 (USA)

VCH

lanthanum, lithium, manganese, neodymium, silver, thorium, yttrium, zinc, and zirconium

2.1. Magnesium–Aluminum Alloys

Aluminum is by far the most important alloying element for magnesium. Its maximum solid solubility in the Mg–Al system is 12.7 wt% at the eutectic temperature 437 °C (Fig. 1). The eutectic contains 32 wt% aluminum, and its composition is $Mg_{17}Al_{12}$. Commercial alloys contain less than 10 wt% aluminum and, according to the equilibrium diagram, should solidify into a homogeneous matrix of magnesium with aluminum in solid solution. This is, however, not the case—a relatively large volume fraction of eutectic constituents is formed (Fig. 2). The solidification diagram shows a distinct plateau at the eutectic temperature (Fig. 3).

Scheil's equation describes freezing under nonequilibrium conditions where solute diffusion is negligible, resulting in a strongly segregated material. The fraction solidified as a function of temperature for equilibrium and nonequilibrium freezing is illustrated in Figure 4 for two Mg–Al alloys. In practice, the Scheil equation provides a reasonable description of solidification during commercial casting processes.

The Mg–Al equilibrium diagram is typical of an age-hardenable system. After solution heat treatment at temperatures just below the eutectic temperature, the β-$Mg_{17}Al_{12}$ phase dissolves, and subsequent quenching gives a supersaturated solid solution. During artificial aging at 150–220 °C, a platelike precipitate forms, resulting in a significant hardening effect. A certain quench

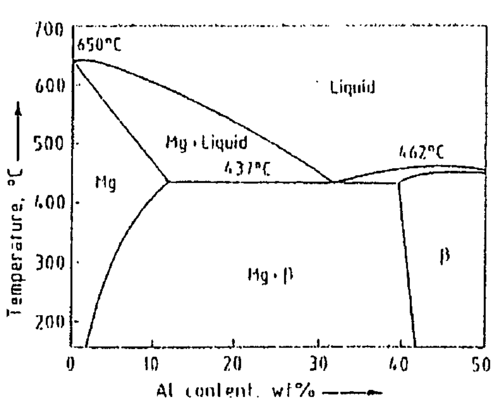


Figure 1. Phase diagram for the binary system Mg–Al

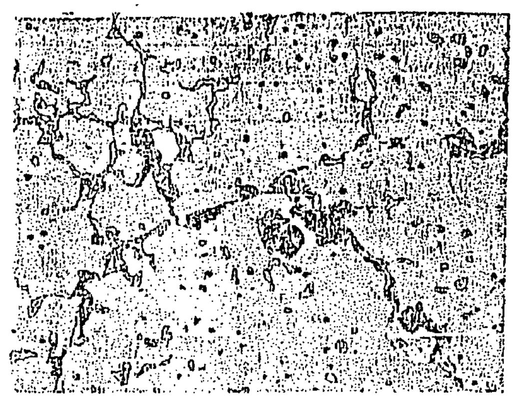


Figure 2. Microstructure of low-pressure die-cast AM100 alloy (× 200)

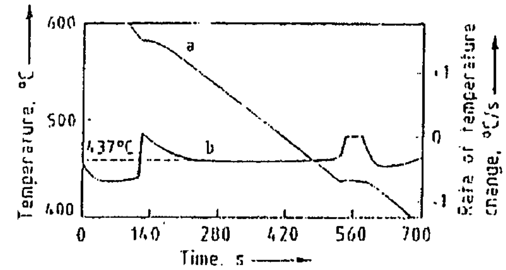


Figure 3. Solidification diagram showing the temperature variation during cooling of the Mg–Al alloy AM 100 A
a) Temperature; b) Rate of temperature change

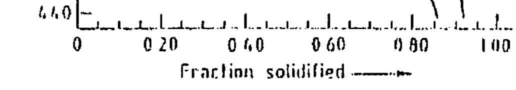


Figure 4. Fraction solidified as a function of temperature calculated for equilibrium and nonequilibrium conditions for two Mg–Al alloys

sensitivity is caused by a competing reaction, whereby the β-phase precipitates discontinuously along grain boundaries. This process occurs during cooling after casting or following solution heat treatment.

ANNEX 3

Table 2B. Chemical Compositions of Alloys

Alloy	Al %	Mn %	Zn %	Ca %	Sn %	Sr %	Si %	Fe %	Ni %	Cu %	Be %
Example 1	4.7	0.29	-	1.9	1.8	0.3	0.01	0.002	0.0006	0.0005	-
Example 2	5.3	0.31	0.3	1.8	0.3	-	0.01	0.002	0.0005	0.0006	0.0005
Example 3	5.1	0.30	-	2.9	1.0	-	0.01	0.003	0.0006	0.0006	-
Example 4	4.9	0.30	-	2.0	2.0	0.3	0.01	0.003	0.0005	0.0005	-
Example 5	5.2	0.31	-	3.1	0.5	-	0.01	0.002	0.0007	0.0004	0.0007
Example 6	6.1	0.29	0.6	2.2	2.0	-	0.01	0.002	0.0006	0.0006	-
Example 7	6.2	0.30	-	2.1	0.5	0.3	0.01	0.003	0.0006	0.0005	-
Example 8	6.2	0.28	-	2.8	1.5	-	0.01	0.003	0.0007	0.0005	-
Example 9	5.9	0.26	-	3.0	0.5	0.3	0.01	0.002	0.0005	0.0006	-
Example 10	6.6	0.25	-	1.9	1.5	0.5	0.01	0.003	0.0006	0.0005	-
Example 11	7.1	0.26	-	2.0	0.5	-	0.01	0.003	0.0006	0.0006	-
Example 12	7.0	0.23	0.8	2.1	2.0	-	0.01	0.002	0.0005	0.0005	-
Example 13	7.3	0.24	-	3.1	0.7	-	0.01	0.003	0.0006	0.0005	0.0004
Example 14	7.1	0.21	0.7	3.0	1.1	-	0.01	0.002	0.0005	0.0005	-
Comparative Example 26	11.8	0.22	0.05	2.9	0.45	0.28	0.01	0.002	0.0009	0.0012	0.0008
Comparative Example 27	12.1	0.19	3.2	-	4.9	-	0.01	0.002	0.0008	0.0011	0.0006
Comparative Example 28	5.9	0.33	0.01	1.15	0.05RE	0.18	0.01	0.003	0.0006	0.0009	0.0008
Comparative Example 29	7.1	0.32	0.74	3.1	0.15RE	0.21	0.01	0.003	0.0009	0.0011	0.0007
Comparative Example 30	8.9	0.23	0.79	0.56	0.2	-	0.01	0.003	0.0009	0.0009	0.0009

Table 3B. Die castability properties of new alloys

Alloy	Metal temperature [°C]	Oxidation resistance	Fluidity	Die sticking	Rank
Example 1	670	10	9	9	91.7
Example 2	690	10	10	8	86.7
Example 3	675	10	9	8	85.1
Example 4	680	10	10	9	93.3
Example 5	670	10	9	9	91.7
Example 6	670	10	9	9	91.7
Example 7	660	10	9	10	98.4
Example 8	660	10	9	10	98.4
Example 9	670	10	10	9	93.3
Example 10	675	10	10	9	93.3
Example 11	660	10	10	9	93.3
Example 12	660	10	10	9	93.3
Example 13	660	10	10	10	100
Example 14	660	10	10	9	93.3
Comparative Example 26	660	10	10	8	87
Comparative Example 27	660	9	10	10	98
Comparative Example 28	680	8	8	5	60
Comparative Example 29	675	10	8	7	75
Comparative Example 30	670	10	10	7	80

Table 5B. Mechanical Properties and Creep Behavior

Alloy	TYS MPa			UTS MPa	E %	CYS MPa			MCR·10^9, S^{-1}		CR mg/cm²/day
	20°C	175°C	200°C	20°C	20°C	20°C	175°C	200°C	150°C, 100 MPa	200°C, 55 MPa	
Example 1	175	160	145	227	5	172	155	143	1.30	1.96	1.52
Example 2	172	158	142	235	5	175	159	146	1.25	1.85	1.50
Example 3	183	165	154	237	4	183	165	155	0.84	1.05	1.58
Example 4	170	161	142	236	6	171	160	143	1.05	1.40	1.48
Example 5	180	168	152	235	4	179	168	153	0.80	1.08	1.56
Example 6	179	165	145	240	5	179	164	147	1.44	2.54	1.38
Example 7	178	163	148	238	5	176	163	146	1.39	2.44	1.45
Example 8	188	170	155	236	5	186	169	155	1.05	1.95	1.37
Example 9	186	172	157	232	4	186	172	157	0.95	1.88	1.49
Example 10	179	162	145	250	5	180	160	146	1.65	4.50	1.54
Example 11	180	160	143	248	5	179	160	142	1.64	4.80	1.32
Example 12	183	165	145	245	4	185	163	144	1.59	4.55	1.45
Example 13	196	170	158	230	3	192	170	157	1.25	2.25	1.47
Example 14	195	174	160	234	3	193	173	161	1.31	2.40	1.32
Comparative Example 26	182	124	95	210	**0.5**	180	120	94	198	289	1.87
Comparative Example 27	198	121	93	274	**2**	197	119	89	322	363	1.84
Comparative Example 28	135	88	68	220	9	131	87	66	102	115	2.29
Comparative Example 29	176	**150**	145	231	**2**	174	152	140	**2.28**	2.67	1.69
Comparative Example 30	166	110	83	228	5	164	105	80	78	92	1.59

ANNEX 4

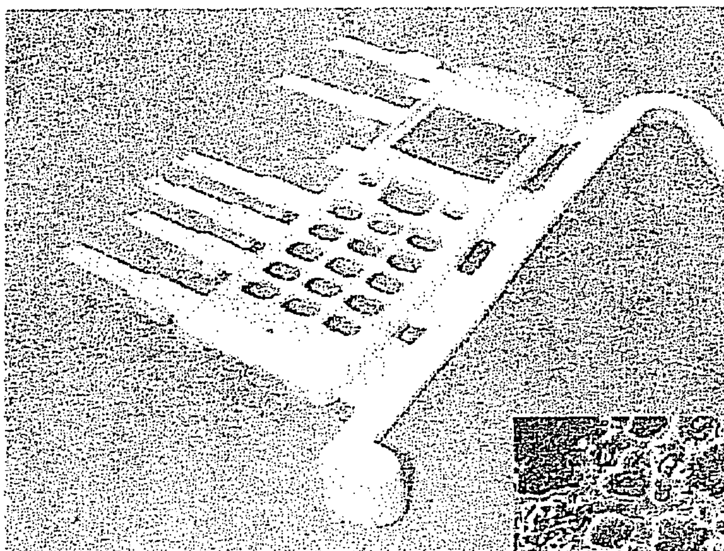
HITACHI Inspire the Next

New Magnesium Alloy

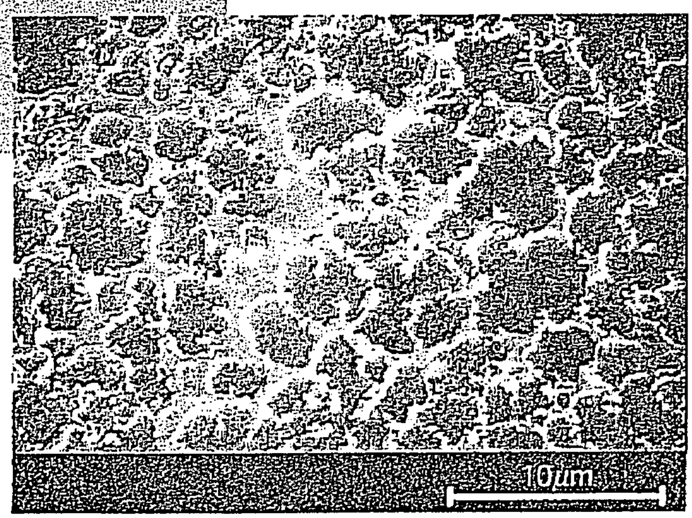
HITMAG™

providing high fluidity

HITMAG is a new Magnesium Alloy developed by HITACHI with a lower melting temperature than AZ91, providing excellent fluidity, high creep strength and corrosion resistance with applications in Thixomolding® and Die Casting.



Thixomolded® Sample using HITMAG



Microstructure of HITMAG

APPLICATIONS

Automotive:

- Housing for Motor, Alternator, etc.
- Transfer Case
- Valve and Engine Cover
- Ignition Key Housing
- Steering Wheel Core
- Instrument Panel
- Seat Frame
- Oil Pan, etc.

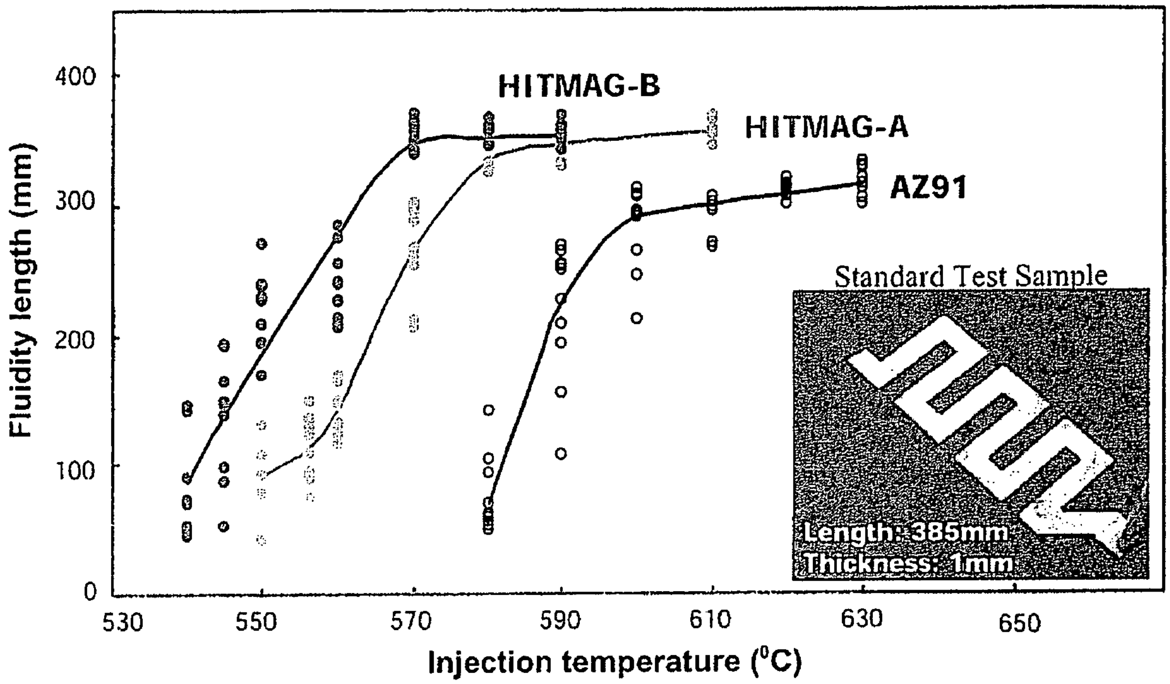
Electronics:

- Digital Camera Body
- PC Projector Body
- Mobile Phone Case
- Laptop Case, etc.

Casting Process:

- Thixomolding®
- Die Casting

Fluidity Characteristics



Material Properties

Physical Properties

Alloy	Liquidus Temperature (°C)	Solidus Temperature (°C)	Density (g/cm^3)	Thermal Conductivity (W/m K)	Specific Heat (J/g K)
AZ91D	598	425	1.81	51.2	1.02
HITMAG-A	567	425	1.92	36.0	0.93
HITMAG-B	556	411	1.96	35.6	0.93

Mechanical Properties*1

Alloy	Vickers Hardness (Hv 50g)	Tensile Strength (MPa)	Proof Stress (MPa)	Elongation (%)
AZ91D	83	265	138	3.4
HITMAG-A	103	264	168	1.5
HITMAG-B	104	301	163	1.6

*1; 0 7mm Sample Thickness

Notes.
Design & specifications are subject to change without notice
Products and company names herein may be trademarks of their owners

Contact Information:
Frank Hunt, Hitachi America Ltd., R&D
34500 Grand River Avenue, Farmington Hills, MI 48335
Ph: (248) 473-6118 E-mail: digital.mfg@hap.com
www.hitachi.us/rd